

DIRECT ANALYSIS OF TUNGSTEN IN CRUDE NIOBIUM PENTOXIDE USING MICROWAVE DIGESTION AND ICP-OES**Gopala Anil, Sivasankaran N. R. Kumar, Arbind Kumar, Manda R. P. Reddy,* and Tirthalli L. Prakash***Centre for Materials for Electronics Technology (C-MET), IDA, Phase-II, HCL Post, Cherlapally, Hyderabad – 500 051, INDIA, Email: mrpreddy@yahoo.com.**Received 09-08-2002***Abstract**

Niobium Pentoxide (Nb_2O_5) is prepared from feed raffinate solution of tantalum solvent extraction. The major impurities, which are associated with niobium pentoxide, are tantalum, tungsten, titanium and iron. While analyzing tungsten by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) niobium interference free lines has to be selected first and this line should also be free from the interference of tantalum, titanium and iron. The interference free line thus selected (224.875nm) has been analyzed for its accuracy and preciseness by analyzing 1 mg/L tungsten doped into 1000 mg/L Nb, 100 mg/L to 500 mg/L Ta, Ti and Fe the results are presented along with a pictorial depiction of spectral interferences by Nb, Ta, Ti and Fe for interference free line selection of tungsten. Nb_2O_5 being ceramic in nature dissolving in open digestion is very difficult and time consuming, here a simple and rapid method of dissolution by microwave digestion (MDS) is adopted.

Introduction

Niobium and tantalum occur together in the nature in the form of mixed oxides. In India, columbite-tantalite mineral occurs in pegmatite found in mica belt of Bihar, Rajasthan and Madhya Pradesh. A good stockpile of this ore is accumulated mainly as a by-product of the mica mining operations in Bihar.¹⁻² The solvent extraction process carries out extraction and separation of niobium and tantalum from the ore. Niobium and tantalum are extracted from a solution of HF using an organic solvent namely tributyl phosphate (TBP). Tantalum is extracted from a solution of 0.5N HF and 2N H_2SO_4 containing tantalum, niobium, iron, tungsten, titanium and other minor constituent elements. Niobium is further extracted from the raffinate solution of tantalum extraction at a concentration of 5N HF and 9N H_2SO_4 . Niobium in the aqueous solution is precipitated as niobium hydroxide, which is then calcined to get Nb_2O_5 . Attempts have been made to prepare niobium electrolytic capacitors by the alkaline earth metal reduction of Nb_2O_5 .³⁻⁴ One of the prerequisites for niobium capacitors is the purity of niobium powder, which is prepared after reduction of Nb_2O_5 . Hence total metallic impurities put together in Nb_2O_5 should be less than 1000 ppm and each elements Fe, Cr,

Ni, K, Na and W should be less than 100 ppm. If these impurities are in excess the dielectric film quality deteriorates and DC leakage current increases. Indian tantalite ores contains appreciable amounts of tungsten. During the solvent extraction of niobium feed, a part of tungsten also gets extracted. Therefore, the final Nb₂O₅ contains appreciable amount of tungsten as impurity. Analysis of tungsten in the Nb₂O₅ resulted in erroneous results because of interferences from matrix element and associated impurities like tantalum, titanium and iron. Tungsten analysis in Nb₂O₅ is carried mostly on 1m-monochromator ICP-OES,⁵ direct solid sampling electrothermal atomic absorption spectrometer⁶ and also some classical techniques involving separation of matrix element.⁷⁻¹¹ A systematic study of line profiling was not reported for the analysis of tungsten in niobium matrix using 0.64m monochromator ICP-OES. Due to the complexity of interference spectra's (Nb, Ta, Fe and Ti) an attempt has been made to identify interference free line to analyze accurately the content of tungsten in presence of tantalum, titanium and iron in Nb₂O₅ with the help of microwave digestion system and ICP-OES. Microwave digestion methods have become a popular technique and are more reproducible, accurate and less time consuming, than conventional digestions on hot plates in open beakers. Microwave digestion keeps blank¹² values low because small volumes of reagent required and allows more samples to be processed per hour than conventional digestion system.

Experimental

Instrumentation

Sample digestion was performed using a microwave digestion system (MDS) Model MLS 1200, Milestone, Italy. The Instrument used for the analysis of tungsten in niobium pentoxide was model JY-24R inductively coupled plasma optical emission spectrometer (ICP-OES), Jobin Yvon, France. A cross flow type of nebulizer (Teflon®) was used for nebulization in the ICP-OES instrument. The instrumental parameters of the ICP-OES and the microwave digestion system with dissolution parameters are given in Table 1 and 2.

Reagents

All chemical used were of suprapure reagent grade from Merck, Germany. The single elemental standard solutions were procured from Merck, Germany. The Nb₂O₅

(Lot –03861R), which is used for validation, was procured from Glen Spectra Reference materials, England. The de-ionized water used was prepared using the nanopure system Barnstead, U.S.A.

Table 1. ICP-OES operating conditions.

<i>Sequential spectrometer</i>	
Spectrometer	Jobin Yvon JY-24R 0.64m Czerny-Turner
Grating	Holographic, 3600 grooves mm ⁻¹
Spectral range	160-500 nm
Slit width	20nm for entrance and exits, adjustable
<i>Plasma</i>	
Plasma torch assembly	Fused quartz with capillary injection
Nebulizer and spray chamber	Cross flow type nebulizer(Teflon®) and Teflon® dual tube spray chamber
Argon Auxillary gas flow rate	1.5 L min ⁻¹
Argon plasma gas flow rate	12 L min ⁻¹
Argon carrier gas flow rate	0.4 L min ⁻¹

Table 2. Operating condition of microwave digestion system.

Frequency	2450 MHz, (equivalent to a wavelength of 12.25cm)	
Power supply	220 Volt/50 Hz-2.2 kW	
Exhaust flow	5 m ³ /minute	
Digestion Program		
Step	Power (Watts)	Time (min)
1	400	2
2	0	2
3	400	2
4	0	2
5	500	2
6	0	2
7	500	2
8	0	5

Sample preparation by Microwave Digestion

A 0.5000g of Niobium Pentoxide was dissolved in the microwave digestion system in a mixture of 5 mL HNO₃, 5 mL of HBF₄ (4HF + H₃BO₃ → HBF₄ + H₂O) and 2 mL of hydrogen peroxide in a Teflon vessel. Eight different sequential steps (Table 2) of microwave heating with intermittent power were applied to control the reaction of the

sample during dissolution. After completing the digestion, the solution was made upto 50 mL in a polypropylene standard flask from Gradplex, Azlon, England before aspirating into the plasma. All samples were prepared in five replicates.

Results and Discussion

Due to the complexity of interference spectra's from Nb, Ta, Ti, and Fe a careful line selection has to be conducted to avoid spectral interferences. A 0.64 m monochromator used here had difficulty in handling complex line rich spectrum of niobium, tantalum, titanium and iron. Spectral scans were performed for each wavelength with 1 mg/L single elemental solutions of tungsten and 1 mg/mL niobium solution. Seven sensitive lines¹³⁻¹⁴ of tungsten were selected (207.911, 209.475, 218.935, 220.448, 222.589, 224.875 and 239.709 nm). Out of seven lines only two lines (207.911 and 224.875 nm) showed no overlap/interference of niobium line. The spectral overlaps are shown in (Figure 1). The rest of the lines showed either direct overlap or wing overlap of niobium line. These two lines (207.911 nm and 224.875 nm) were checked for interference of tantalum, titanium and iron line by profiling with 100 mg/L single elemental standard solution. The line 207.911 nm had no titanium and iron interference but a small left wing overlap and a right big wing overlap of tantalum were found hence it is not suitable for analysis of tungsten. It was found that 224.875 nm line was free from titanium and tantalum line interference but iron had a left wing overlap only hence this line was used for analysis of trace tungsten.

The spectral overlaps are shown in (Figure 2). In order to analyze tungsten, the line 224.875 nm was chosen, and it was found that upto 500 mg/L of iron with right background subtraction gave accurate results. To validate the ICP-OES methodology a standard addition of iron tantalum and titanium of different concentrations (100, 200, 300, 400 and 500 mg/L) added into 1000 mg/L niobium solution, this was doped with 1 mg/L tungsten. The results of tungsten analyzed were found to be well within the limit of accuracy, which is given in Table 3. A typical analysis of crude and purified Nb₂O₅ prepared at our laboratory is given in Table 4. Nb₂O₅ being ceramic in nature, it was very difficult to achieve complete dissolution in open hot plate condition. A simplified microwave digestion procedure with intermittent cooling was designed so that the pressure build up did not arise very fast. The dissolution was achieved in eight steps of

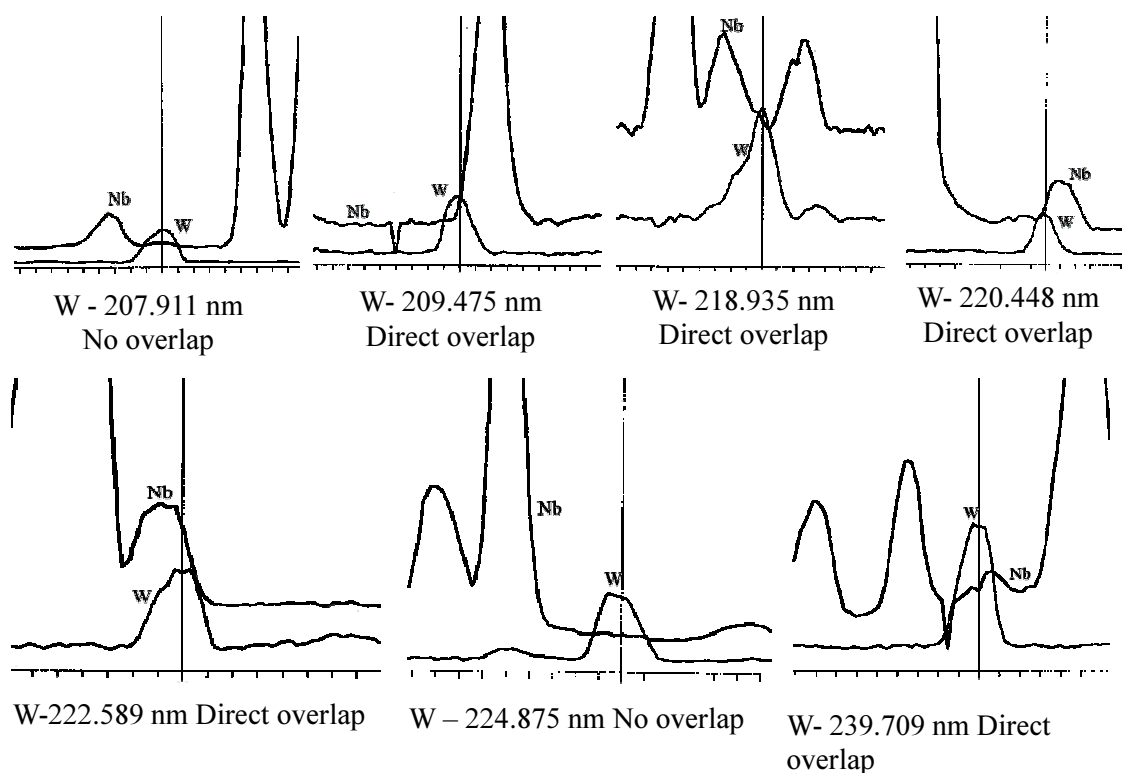


Figure 1. 1 mg/mL of niobium overlapped with 1 mg/L tungsten.

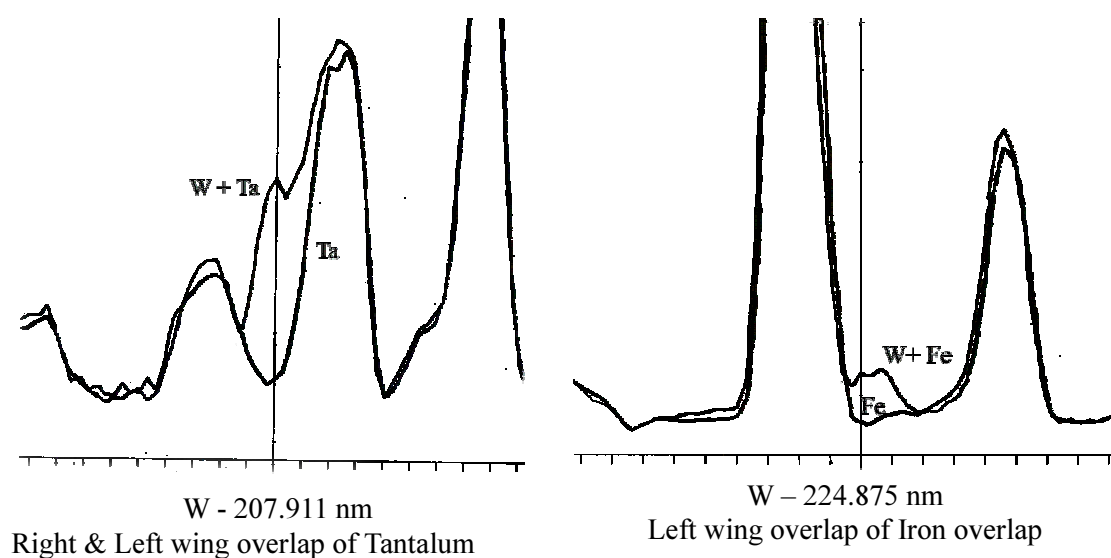


Figure 2. Spectral overlaps of tantalum and iron 100 mg/L with added 1 mg/L of tungsten in it.

cooling and microwave heating as detailed in Table 2. To validate the microwave digestion of Nb₂O₅ and the analysis of tungsten, 0.500 g of Nb₂O₅ (Lot –03861R), procured from Glen Spectra Reference materials, England was taken in triplicate. Sample 1 was used as blank, Sample 2 was doped with 500 mg/L of Ta, Ti and Fe and 0.5 mg/L of tungsten and Sample 3 was doped with 500 mg/L of Ta, Ti and Fe and 1.0 mg/L of tungsten and subjected to microwave dissolution as in Table 2. After dissolution the solutions was made upto 50 mL. The results of tungsten show a recovery in the range of 99 to 101% is given in Table 5. The detection limit of tungsten thus calculated as 3s of the blank was found to be 0.031 mg/L for pure tungsten solution and 0.221 mg/L for tungsten in presence matrix (0.5 g/50 mL of Nb₂O₅) and 0.234 mg/L in presence of 500 mg/L of Ta, Ti, Fe and matrix.

Table 3. Standard addition and recovery of tungsten.

S. No.	Standard Addition	Recovery of tungsten (224.875 nm) in mg/L (SD)
1.	1 mg/L Tungsten + Niobium 1000mg/L +100 mg/L Tantalum, Titanium and Iron	1.02±0.008
2.	1 mg/L Tungsten + Niobium 1000mg/L +200 mg/L Tantalum, Titanium and Iron	1.01±0.007
3.	1 mg/L Tungsten + Niobium 1000mg/L +300 mg/L Tantalum, Titanium and Iron	1.03±0.011
4.	1 mg/L Tungsten + Niobium 1000mg/L +400 mg/L Tantalum, Titanium and Iron	1.02±0.009
5.	1 mg/L Tungsten + Niobium 1000mg/L +500 mg/L Tantalum, Titanium and Iron	1.02±0.008

SD: Standard Deviation of five readings.

Table 4. Typical analysis of Nb₂O₅ prepared at C-MET, Hyderabad.

S. No.	ELEMENTS	Crude Nb ₂ O ₅ (in %) (SD)	Purified Nb ₂ O ₅ (in %) (SD)
1.	Tantalum	2.240±0.121	0.070±0.007
2.	Iron	1.535±0.078	0.005±0.0003
3.	Titanium	0.585±0.015	0.002±0.0001
4.	Tungsten	0.621±0.035	0.071±0.008

SD: Standard Deviation of five readings.

Table 5. Microwave digestion of doped Nb₂O₅ and recovery.

S.No.	Doped Samples of Nb ₂ O ₅	Recovery % of Tungsten (SD)
1	Nb ₂ O ₅ doped with 0.5mg/L of W and 500mg/L of Ta, Fe and Ti	98.86±0.32
2.	Nb ₂ O ₅ doped with 1.0mg/L of W and 500mg/L of Ta, Fe and Ti	101.34±0.85

(S.D): Standard Deviation of five readings.

Conclusion

Generally direct analysis of tungsten in Nb₂O₅ was difficult without matrix/interferent separation using a 0.64 m monochromator with ICP-OES. The present method developed with a systematic line profiling can be applied successfully in analyzing accurately the content of tungsten in presence of tantalum, titanium and iron in Nb₂O₅. The complete dissolution of Nb₂O₅ was achieved very easily by microwave digestion procedure. The method is rapid accurate and could be successfully applied for the analysis of Nb₂O₅.

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Povzetek

Niobijev pentoksid (Nb_2O_5), dobljen iz rafinata pri ekstrakciji tantala, vsebuje nečistoče kot so tantal, volfram, titan in železo. Zato moramo pri analizi volframa z ICP-OES izbrati takšno spektralno črto, kjer so spektralne interference elementov, ki so prisotni v analizirani raztopini, zanemarljive. Ugotovili smo, da je takšna spektralna črta pri 224.875 nm. Pri tej valovni dolžini smo tudi določili točnost ter natančnost postopka z analizo volframa, ki je bil prisoten v koncentraciji 1000 mg/L v raztopini, ki je vsebovala še interferenčne elemente Nb, Ta, Ti in Fe v koncentracijskem območju od 100 do 500 mg/L. Ker se Nb_2O_5 počasi in težko raztaplja s kislinami v odprtem sistemu, smo razvili postopek za njegovo raztapljanje v mikrovalovni peči.